INTERLABORATORY STUDY 90-2

N-NITROSODIMETHYLAMINE IN REAGENT WATER AND SEWAGE INFLUENT

APRIL 1991

Ontario
Environment
Environnement

ISBN 0-7729-8261-9

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Report prepared for:

Laboratory Services Branch
Ontario Ministry of the Environment

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Cette publication technique
n'est disponible qu'en anglais

PIBS 1548

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Table of Contents

1 SUMMARY AND CONCLUSIONS

The detection of N-Nitrosodimethylamine (NDMA) in the drinking water supply of Elmira, Ontario occurred in 1989. As this was an organic compound that had previously not been tested for under routine conditions, there quickly developed a need for an accurate and reliable method for NDMA analysis in various aqueous matrices. The Quality Management Unit of Environment Ontario's Laboratory Services Branch agreed to conduct several interlaboratory studies to assess the interlaboratory comparability for the analysis of NDMA in water and wastewater.

Interlaboratory Study 90-2 was designed to assess the interlaboratory variability for the analysis of NDMA in spiked reagent water (low levels) and spiked waste treatment plant effluent/influent (high levels). The study was divided into two parts, based on the matrices. The results from the first set of analyses in the spiked reagent water (Part A) indicated a greater degree of variability than was expected. This part of the study was repeated (Part B) and also included a linearity study. These results showed an improvement (decrease in interlaboratory variability) in the results from the participants. The linearity study demonstrated that the High Resolution Mass Spectrometry (HRMS) method was linear, the Low Resolution Mass Spectrometry (LRMS) method could be linear when calibrated correctly, and the Thermal Energy Analyzer (TEA) method was variable.

The results from the analyses for NDMA in a sewage treatmwent plant influent matrix (Part C) demonstrated considerable variability among the participants. Not all of the participating laboratories reported results, so the data set was incomplete. The results did not indicate that one method was better able to achieve the target results. Further method development was indicated for the participating laboratories. A repeat study was scheduled for November 1990, distributed as Interlaboratory Study 90-7, and reported separately.

The results from the three parts of the study also demonstrated that close attention to the ratio of d6-NDMA to native NDMA in the sample is required to produce accurate results when using the method of isotope dilution.

2 INTRODUCTION

In 1989, Environment Ontario personnel detected of N-Nitrosodimethylamine (NDMA) in the drinking water supply of Elmira, Ontario (1) and later in the effluent of the municipal waste treatment plant. As NDMA is a suspected carcinogen (2,3), there was an immediate need for accurate and reliable monitoring of the various aqueous matrices for NDMA. Various government, industrial, and commercial laboratories developed analytical methods for the analysis of NDMA in drinking water and effluents. In early 1990, the Quality Management Unit (QMU) of Environment Ontario's Laboratory Services Branch (LSB) was asked to evaluate the comparability of data from these laboratories. Two studies would be required. The first to assess the interlaboratory variability for the analysis of NDMA in reagent water. The second would assess the interlaboratory variability in an effluent/influent matrix.

Interlaboratory Study 90-2 was intended to assess the interlaboratory comparability for NDMA analysis at low levels (near the US EPA Drinking Water Criteria of 0.014 µg/L (4)). Participating laboratories received spiked reagent water samples for analysis. The results from this study (Part A) indicated significant bias among the laboratories (see Section 4.1). This study was repeated in an effort to reduce the biases among laboratories. It included a linearity study of calibration standards as well as the spiked reagent water samples (Part B).

The final stage of Interlaboratory Study 90-2 (Part C) consisted of spiked sewage treatment plant influent samples for the analysis of NDMA. The spiking level for two of the samples was chosen to bracket the maximum level of NDMA allowed to be present in effluents discharged to the Elmira Sewage Treatment Plant (5).

The following sections describe the sample preparation procedures for each part of the study, the sample distribution procedure and the data handling techniques. Each part of the study is discussed separately in the Discussion section with a final summary of the study included at the end.

3 PROCEDURE

3.1 SAMPLE PREPARATION

3.1.1 STOCK SPIKING SOLUTION

The stock spiking solution was prepared from a concentrated NDMA solution of 97 µg/mL NDMA in ethanol. This solution, certified by the supplier as traceable to USDA Reference 7 Nitrosamine Standard, was obtained from Thermedics Inc., Woburn MA, Lot #322-69. A spiking solution was prepared by diluting the concentrated stock solution in methanol. The volumetric flask containing the dilute solution was stored overnight in a freezer at -20°C. The solution was sealed into amber 5 mL ampoules the following day. The ampoules were stored at 4°C in the dark. This ampouled solution was used to prepare the spiked samples in all three parts of Interlaboratory Study 90-2.

3.1.2 PART A

Prior to sample preparation, a batch of 1 litre, amber, glass bottles was rinsed with ultra-pure HPLC reagent water. Four empty bottles were randomly selected from the batch to be used for the study and weighed to the nearest 0.1 g. All of the bottles were filled to approximately 1 cm from the top with distilled, deionized water from the LSB building supply. These samples were labelled N1, N2, N3, and N4. N1 was designated the "blank" and filled to the top with reagent water. Samples N2, N3, and N4 were spiked with the appropriate amount of NDMA spiking solution that had been warmed to room temperature, using the appropriate size of gas-tight microlitre syringe. The bottles were then carefully filled to the top with reagent water and capped. The bottles were mixed on a bottle rotator for approximately 15 minutes. Four bottles were then randomly selected and weighed to the nearest 0.1 g (Final weights varied by ±5.0 g). The mean weight of the empty and filled bottles was used to calculate the final volume and thereby calculate the expected values for the spiked samples.

The results from the first two laboratories reporting back, indicated background levels of NDMA that were higher than the spiking levels. The source of contamination was tracked to a new resin bed that had been installed in the building's distillation unit one week previously. All the participants were notified of this contamination and were not required to analyze the samples.

A new set of samples was prepared using ultra-pure HPLC water. The same preparation procedure was used as described above. The bottles were labelled NA1, NA2, NA3, and NA4 and distributed to the participants. The results from these samples are reported as Part A.

3.1.3 PART B

The second part of Interlaboratory Study 90-2 consisted of spiked reagent water samples and an ampoule to be used for a linearity study. The spiked reagent water samples were prepared in the same manner as used for Part A. The samples were labelled NB1, NB2, NB3, and NB4. Six bottles were randomly chosen to be weighed before and after spiking to calculate the final volume and thereby calculate the target levels of NDMA.

The ampoule used for the linearity study was from the same stock used by the QMU to prepared the spiked samples. Each participating laboratory received one 5 mL amber ampoule and was instructed to spike 800 mL of pure reagent water with the following aliquots of the spiking material: 20 µL, 100 µL, 500 µL, 700 µL, and 1000 µL. The participants were also requested to analyze a reagent water blank with the above spiked samples.

3.1.4 PART C

The third part of Interlaboratory Study 90-2 consisted of spiked matrix samples. The matrix chosen was the town-line influent to the Elmira sewage treatment plant. Approximately 40 litres of influent was collected on June 13, 1990 in amber glass bottles. The influent was mixed in a 50 litre stainless steel drum at the laboratory and stirred overnight to homogenize the bulk sample. Coarse particles were filtered out using cheesecloth.

To confirm that influent samples that had been spiked with NDMA were reasonably stable at room temperature for 48 hours (potential shipping delay by the courier), a small stability study was performed. Two one litre portions of influent were spiked with different levels of NDMA. The amber glass bottles containing the samples were stored at room temperature in a dark cupboard for 48 hours before submitting for analysis. The results were as follows:

Sample 1	Target: 0.122 µg/L	Reported: 0.11 µg/L
Sample 2	Target: 0.47 µg/L	Reported: 0.48 µg/L

The above results demonstrate that the spiked samples should remain stable at room temperature even if there was a shipping delay of 48 hours.

The influent samples were prepared in the same manner as the reagent water samples in Parts A and B. To minimize the risk of non-homogeneity to each participant, the sample sets were filled in sequence, i.e. the first four bottles were labelled NC1, NC2, NC3, and NC4 and were sent to the first participant, the next four bottles were labelled NC1, NC2, NC3, and NC4 and sent to the next participant, etc.

The spiking levels of these samples were designed to assess the analytical capability of the participants at the legal discharge limit of 0.500 µg/L of NDMA (5). Target levels were close to or above this amount. All spiking was done with the appropriate microlitre syringe. Nine bottles were chosen at random before and after spiking to calculate the final volume of sample and thereby calculate the target levels of NDMA.

3.2 SAMPLE DISTRIBUTION

Samples were cooled, packed in cardboard cartons that were lined with styrofoam chips, and shipped via Purolator Courier. Samples for Part A were distributed on March 14, 1990. Samples for Part B were distributed on April 30, 1990. Samples for Part C were distributed on July 9, 1990.

3.3 DATA HANDLING

Participants received a report form with all samples sets. Results were entered into an electronic spreadsheet. The mean, median, and standard deviation were calculated for each sample. Results were also converted to percent recovery of the design value. All results are included in Appendix 1.

For the linearity study in Part B, the results were entered into an electronic spreadsheet and the best fit line was calculated using linear regression. Two lines were fitted to each participant's results, one using a linear equation and one using a quadratic equation. The graphs from each participant, showing both equations, are included in Appendix 1. A table of the regression statistics for each participant is also included in Appendix 1.

The results for Part C were converted to percent recovery of the design value after subtracting the value reported by each participant for the unspiked influent from the results reported by each participant for the spiked influent samples. These results are included in Table 8, Appendix 1.

As an aid to assess the within laboratory performance, the results for the spiked samples from each participant were plotted using the Youden two-sample technique (6). The first graph for each part of the study has the low spike plotted versus the mid-range spike. The second graph for each part of the study has the mid-range spike plotted versus the high spike. The results are expected to cluster around the design value. A 45° line drawn between the origin and the design value can be used to indicate the target within-laboratory precision. Results that are on or close to the 45° line indicate good within-laboratory precision. Results that fall on this line but are higher or lower than the design value indicate a bias. These graphs are included in Appendix 1.

4 RESULTS AND DISCUSSION

4.1 PART A

Results were received from all eight participants for the spiked samples prepared in ultra-pure HPLC water, and are summarized in Table 1 of Appendix 1. Each participant provided information regarding their sample preparation principles and their instrumental preparation principles. All the participants used dichloromethane as the extraction solvent. The instrumentation used by each participant is also listed in Table 1. The results converted to percent recovery of the design value are given in Table 2.

Laboratory 8004 analyzed their sample extracts twice, using two different capillary gas chromatographic columns. Both sets of results are include in Table 1. Laboratory 8007 used two different analytical techniques. They extracted two aliquots of each sample, then analyzed one aliquot using gas chromatography with Low Resolution Mass Spectrometry (GC/LRMS) and analyzed the other aliquot using gas chromatography with a Thermal Energy Analyzer (GC/TEA). Laboratory 8007 then reported a second set of results for these samples. Their standard solution appeared to have been contaminated, so they recalculated their results. Both sets of results as reported are included in Table 1.

The results from this study indicate a significant bias among the participants. The results indicate a probable difference in the relative accuracy of the NDMA and deuterated NDMA (d_6-NDMA) in use among the participants. There are also differences in chromatographic and instrumental methodology which may contribute to these biases.

Two laboratories, 8001 and 8003, over-recovered the samples by 15-33%. Two laboratories, 8004, GC column 2 and 8007(GC/LRMS), under-recovered by up to 30%. The results from Laboratories 8002, 8005 and 8008 were erratic. Only the results from 8004, GC column 1, and 8006 were consistent and reasonably close to the design values.

The differences between the laboratories do not appear to be directly method-dependant. The variable results produced by laboratories 8002, 8005, and 8008 were from three different detectors.

There is good agreement between the mean and median for all three samples, suggesting that the data sets are not skewed in one direction. However the variability in the results is not acceptable, particularly for the low-level sample (NA2 Standard Deviation equals 73%).

The Youden two-sample plots (Figures 1 and 2) clearly demonstrate the variability in results from laboratories 8005, 8007 (first set of reported results; see above) and 8008. There appears to be a greater degree of within-laboratory variability for all participants when analyzing at lower concentrations (Figure 1).

The variability of results from this study indicated a need to repeat this study in the hope that the participating laboratories would show better agreement for the analysis of NDMA in reagent water. As well, there was concern that the variability of some of the participants indicated curvature of the calibration curve. The repeat study of the spiked reagent water samples was scheduled for the end of April 1990 and included an ampoule for the participants to prepare spiked samples at specified concentrations for a linearity study.

4.2 PART B

One of the participants in Part A chose not to participate any further in the MOE Interlaboratory Studies for NDMA. Two new participants were included for Part B. Results for the spiked reagent water samples were received from all of the participants and are given in Table 3. The results converted to percent recovery of the design value are given in Table 4. Results for the linearity study were received from only 8 of the participants and are given in Table 5. All the results from the linearity study are plotted in Figures 5-13. The regression statistics are given in Table 6.

Laboratory 8006 received the samples on May 1, 1990 with NB2 broken and the NB1 bottle very badly cracked. A second set of samples was shipped immediately and they arrived intact. Laboratory 8006 analyzed all of the samples received, and analyzed the second set of samples in duplicate. They qualified their results for the first bottle of NB1, due to its damaged condition. All the results are reported in Table 3.

Laboratory 8007 requested two sets of samples. One set was analyzed using GC/LRMS. The second set was analyzed using GC/TEA. The former set of results are designated as 8007A in Tables 3 and 4, and the latter set of results are designated as 8007B in Tables 3 and 4.

Spiked Reagent Water Samples

The findings from Part B reaffirm the findings from Part A. The laboratories do tend to show slightly better agreement with the design values. The variability has been reduced for the low level sample (Standard Deviation for NA2 = 73%, Standard Deviation for NB2 = 43%).

The results from this study appear to be more method-dependant than the previous study. The results from the two of the laboratories using GC/HRMS (8001 and 8006) show more consistent accuracy across the whole range than the other two methods. Laboratory 8010 also used GC/HRMS, but it appears that their standard differs from the spiking material and from the other participants' standards. The results from the laboratories using GC/LRMS (8002, 8003, 8004, 8007A, and 8009) demonstrate less consistent accuracy across the analytical range. Some of these participants demonstrate good agreement with the design values for the low and middle spikes (NB2 and NB3), but are biased low or high for the high spike (NB4). Other participants show the reverse trend, having good agreement with the middle and high spikes (NB3 and NB4) and biased low or high results for the low spike (NB2). The results from the two participants using GC/TEA are more variable. While laboratory 8007B's results are fairly consistent, they are biased high. The results from laboratory 8005 are quite variable.

The Youden two-sample plots also demonstrate the different grouping of the participants, depending on the analytical range. The participants whose results are close to the design value and the target line of precision in Figure 3 (low and mid-range spikes) are not the same participants that are close to the design value and the target line of precision in Figure 4 (mid-range and high spikes).

Linearity Study

In the linearity study, three of the participating laboratories, 8001, 8006, and 8009, provided essentially linear data, with very good fit to the line and a slope very close to the expected. They included laboratories using High Resolution Mass Spectrometry (HRMS) and Low Resolution Mass Spectrometry (LRMS).

The results from laboratories 8002, 8004, and 8007A (GC/LRMS) demonstrate curvature and a quadratic fit to the line. Laboratories 8002 and 8004 also demonstrate a high bias of 30-60% at the 1.00 µg/L level.

The results from laboratory 8007B (GC/TEA) gave a good fit to the line but were quite erratic (Figure 12). The other laboratory using GC/TEA (8005) demonstrated a more consistent fit to the line but demonstrated a low bias at the 1.00 µg/L level of about 15% (Figure 9).

There does not appear to be a direct correlation for the individual laboratory's bias when comparing the results for the spiked reagent water samples to the results for the linearity study. Laboratories that over-recovered for the high spike (NB4), produced results that showed excellent agreement with the design values for the two high spikes (DIL#4 and DIL#5) in the linearity study. There was no pattern in the results at the mid-range. Participants may have had good recovery for sample NB3 and differed considerably from the target for DIL#2, or vice versa. Only for the low spike (NB2) and the lowest dilution level (DIL#1) was there any degree of agreement. Generally, the participant who reported a result close to the target for DIL#1 also had good recovery for NB2. A biased result (high or low) for DIL#1 generally had a corresponding high or low result for NB2.

The results from Part A and Part B indicate that the GC/HRMS procedure is linear, and is capable of accuracy. The GC/LRMS procedure tends to show curvature but can be linearized and calibrated to achieve accuracy. The recovery appears to be more variable for the GC/LRMS and GC/TEA methods. The between laboratory variability improved from Part A to Part B, though the participants are encouraged to participate in future intercomparisons so as to reduce the between laboratory variability. The need to determine the variability among the laboratories for the analysis of NDMA in effluent matrices made it necessary to proceed to the second phase of the original design of this interlaboratory study. Sample distribution was scheduled for July 1990.

4.3 PART C

Three of the participants did not report results for this part of the study. One of the participants explained that they had a new instrument (GC/LRMS) on which they had attempted to analyze the samples, but that difficulties with the new equipment resulted in difficulties with the analyses, and the samples were exhausted without producing any reportable values. The other two participants did not explain the lack of any reportable results.

Laboratory 8001 noted that they had changed their spiking level for the d_6-NDMA added to the effluent samples compared to the levels used in the previous two studies. Further internal method development work had demonstrated that a 1:1 ratio of d_6-NDMA to NDMA in the sample gave more accurate results. Higher levels of d_6-NDMA were added to the samples in Part C.

Laboratory 8004 added several qualifying remarks to their results. Interferences in the matrix resulted in peak broadening and generally poor chromatography on both of their columns. The matrix interference on the two columns results in poor agreement, with no one column appearing to show better results than the other. The results reported were based on the following protocol: when the results from the two columns differed by more than 20% and neither column showed an obvious interferent different from the other, the lower of the two results was reported. Sample

NC4 was over roto-evaporated, resulting in a low recovery of their D_6-NDMA surrogate standard. The low recovery was below their acceptable QA/QC criteria of 5%, so no result was reported. Had these been routine samples from a client, Laboratory 8004 would not have reported these results, but recommended resampling and an adjustment to their extraction procedure to attempt to minimize matrix interferences.

Laboratory 8006 noted that they had had a magnet stability problem with their instrument, causing frequent drift problems, so they were not as confident with the results for these samples as they had been for Part B. They also modified their extraction procedure by using a Kuderna-Danish column rather than a rotary evaporator. They also used different levels of D_6-NDMA for the surrogate standard in each sample.

Laboratory 8009 noted that they used a higher level of D_6-NDMA for the surrogate spike in the influent samples for Part C than they had used for the reagent water samples in Part B.

The results for the spiked influent samples were more variable than for the spiked reagent water samples in Parts A and B. The data sets are not normally distributed, particularly for NC4, as the interlaboratory mean and median do not agree. The mean and median also do not show good agreement with the design value.

Only two of the participants achieved results that were close to the design values (8001 and 8009). One laboratory used HRMS and the other used LRMS, so it does not appear as if one detection system is more suitable than the others for NDMA analysis in influents, based on these results. However, the low recovery relative to the design value reported by the other participants suggests that they are not as familiar with the analysis for NDMA in influents and further development work is required.

Most of the participants demonstrated reasonable within-laboratory precision, except for Laboratory 8004. The paired results in Figures 14 and 15 are close to the line of target precision, except as noted above. Laboratory 8004 did not report a result for sample NC4, so they appear to have very poor precision in Figure 15. However their results for NC2 and NC3 plotted in Figure 14 demonstrate problems with their within-laboratory precision for the influent samples. This reflects their qualifying remarks to their results as noted above.

The variable performance for the analysis of NDMA in an influent indicated that the participating laboratories needed to undertake further development of their methods. There was no clear indication that any one method was more appropriate for this analysis, based on this study. A repeat study was recommended, using several different effluent/influent matrices, if possible. This study was scheduled for November 1990 and distributed as Interlaboratory Study 90-7.

4.4 Summary of Interlaboratory Study 90-2

Interlaboratory Study 90-2 was designed to assess the interlaboratory variability for the analysis of NDMA in spiked reagent water (low levels) and spiked effluent/influent (high levels). The study was divided into two parts, based on the matrices. The results from the first set of analyses in the spiked reagent water (Part A) indicated a greater degree of variability than was expected. This part of the study was repeated (Part B) and also included a linearity study. These results showed an improvement (decrease in interlaboratory variability) in the results from the participants. The linearity study demonstrated that the HRMS method was linear, the LRMS method could be linear when calibrated correctly, and the TEA method was variable.

The results from the analyses for NDMA in an influent matrix (Part C) demonstrated considerable variability between the participants. Not all of the participating laboratories reported results, so the data set was incomplete. The results did not indicate that one method was better able to achieve the target results. Further method development was indicated for the participating laboratories. A repeat study was scheduled for November 1990, distributed as Interlaboratory Study 90-7, and reported separately.

The Youden plots for Parts A and B (samples NA4 vs. NA3 and samples NB4 vs. NB3 respectively) showed a tendency for several laboratories to fall along a line parallel to the expected line through the design value. In Part C, where several analysts increased the spiking level of d_6-NDMA to be closer to the expected level of NDMA in the high sample, this pattern is less apparent. The accuracy of estimating the amount of NDMA present in a sample requires attention to the ratio of d_6-NDMA to native NDMA.

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6 APPENDIX 1: TABLES AND GRAPHS

TABLE 1: INTERLABORATORY STUDY 90-2, PART A

(Results in µg/L)

CODE	NA1	NA2	NA3	NA4	DETECTOR
DESIGN	Blank	0.020	0.098	0.980	-
8001	<0.002	0.023	0.121	1.330	GC/HRMS
8002	<0.010	0.007	0.081	0.990	HRGC/LRMS
8003	<0.001	0.023	0.110	1.300	GC/LRMS
8004C1	ND	0.0219	0.0954	0.9321	GC(RTX-5)/LRMS
8004C2	ND	0.0153	0.0778	0.7005	GC(RTX-35)/LRMS
8005	<0.020	0.035	0.050	1.040	GC/TEA
8006	<0.006	0.018	0.111	1.200	GC/HRMS
8007A1	0.005	0.012	0.064	0.725	GC/LRMS
8007A2	0.006	0.015	0.083	0.934	GC/LRMS
8007B1	ND	0.029	0.061	0.732	GC/TEA
8007B2	ND	0.033	0.069	0.828	GC/TEA
8008	ND	0.063	0.120	0.090	GC/ITD
MEAN		0.0246	0.0869	0.9001	
MEDIAN		0.0225	0.082	0.9331	
STD DEV		0.0147	0.0242	0.3337	

NOTE: Laboratory 8004 used two different GC analytical columns on the same extract and thus two sets of results are presented (C1 and C2). Laboratory 8007 provided four sets of results. 8007A and 8007B represent two different instrumental detectors. Numbers 1 and 2 represent two different dates of analysis.

LEGEND:
GC/HRMS: Gas chromatograph, high resolution mass spectrometer
GC/LRMS: Gas chromatograph, low resolution mass spectrometer
HRGC/MS: High resolution gas chromatograph, low resolution mass spectrometer
GC/TEA: Gas chromatograph, thermal energy analyzer
GC/ITD: Gas chromatograph, ion-trap detector

TABLE 2: INTERLABORATORY STUDY 90-2, PART A

Results Converted to Percent Recovery of Design Value

CODE	NA2	NA3	NA4
DESIGN	0.20 µg/L	0.098 µg/L	0.980 µg/L
8001	115%	123%	136%
8002	35%	83%	101%
8003	115%	112%	133%
8004C1	110%	97%	95%
8004C2	76%	79%	71%
8005	175%	51%	106%
8006	90%	113%	122%
8007A1	60%	65%	74%
8007A2	75%	85%	95%
8007B1	145%	62%	75%
8007B2	165%	70%	84%
8008	315%	122%	9%
MEAN	123%	89%	92%
MEDIAN	112%	84%	95%
STD DEV	73%	25%	34%

TABLE 3: INTERLABORATORY STUDY 90-2, PART B

(Results in µg/L)

CODE	NB1	NB2	NB3	NB4	DETECTOR
DESIGN	Blank	0.0164	0.0904	0.822	
8001	0.001	0.017	0.098	0.980	HRMS
8002	<0.010	0.0103	0.0753	0.8543	LRMS
8003	<0.002	0.0187	0.106	1.050	LRMS
8004	ND	0.0247	0.0834	0.8105	LRMS
8005	<DL	0	0.092	1.157	TEA
8006A 8006B 8006C	0.006 0.007	 0.010 0.012	0.099 0.093 0.103	0.809 0.819 0.822	HRMS
8007A	ND	0.017	0.084	0.926	LRMS
8007B	ND	0.022	0.104	1.015	TEA
8009	ND	0.020	0.110	0.690	LRMS
8010	0.001125	0.021	0.164	1.109	HRMS
MEAN		0.0157	0.1010	0.9202	
MEDIAN		0.0170	0.0985	0.8902	
STD DEV		0.0071	0.0224	0.1423	

NOTE: Laboratory 8006 received a second set of sample due to breakage. All samples were analyzed. The first set were designated "A". The second set was analyzed in duplicate and designated "B" and "C". Laboratory 8007 analyzed the samples on two different instrumental detectors, designated "A" and "B".

LEGEND: HRMS: High resolution mass spectrometer
LRMS: Low resolution mass spectrometer
TEA: Thermal energy analyzer

TABLE 4: INTERLABORATORY STUDY 90-2, PART B

Results Converted to Percent Recovery of Design Value

CODE	NB2	NB3	NB4
DESIGN	0.0164 µg/L	0.0904 µg/L	0.822 µg/L
8001	104%	108%	119%
8002	63%	83%	104%
8003	114%	117%	128%
8004	151%	92%	99%
8005	0%	102%	141%
8006A		110%	98%
8006B	61%	103%	100%
8006C	73%	114%	100%
8007A	104%	93%	113%
8007B	134%	115%	123%
8009	122%	122%	84%
8010	128%	181%	135%
MEAN	88%	112%	112%
MEDIAN	104%	109%	108%
STD DEV	43%	25%	17%

TABLE 5: INTERLABORATORY STUDY 90-2, PART B; LINEARITY STUDY

(Results in µg/L)

LAB CODE	BLANK	DIL#1	DIL#2	DIL#3	DIL#4	DIL#5
TARGET	0	0.02125	0.10625	0.53125	0.74375	1.0625
8001	0	0.021	0.120	0.650	0.840	1.270
8002	0	0.0168	0.0846	0.5653	0.8745	1.3869
8003	0	0.021	0.114	0.640	0.913	1.320
8004	0	0.0555	0.1246	0.7537	1.0423	1.6657
8005	0	0.0196	0.1072	0.4429	0.6963	0.898
8006	0.003	0.025	0.114	0.553	0.744	1.007
8007B	0	0	0.240	0.340	0.760	1.060
8007A	0	0.010	0.060	0.480	0.690	1.060
8009	0	0.025	0.105	0.495	0.680	0.995

TABLE 6: INTERLABORATORY STUDY 90-2, PART B; LINEARITY STUDY

Regression Statistics

LAB CODE	QUADRATIC REGRESSION			LINEAR REGRESSION		
	CONSTANT	R SQUARED	X COEF. X COEF^2	CONSTANT	R SQUARED	X COEF.
8001	-0.37616	0.998414	1.149862 0.000034	-3.02031	0.998349	1.184227
8002	-3.52526	0.999917	0.844585 0.000438	-36.8368	0.991152	1.277533
8003	-4.99577	0.999933	1.182615 0.000062	-9.71312	0.999746	1.243926
8004	12.23290	0.998918	1.136272 0.000388	-17.2435	0.994052	1.519375
8005	-.067783	0.995778	0.947505 -0.00008	6.673937	0.995018	0.861645
8006	0.602696	0.999967	1.124528 -0.00016	13.26062	0.997711	0.960014
8007B	38.66676	0.953775	0.589583 0.000361	11.21875	0.943451	0.946323
8007A	-9.77921	0.999463	0.802230 0.000192	-24.4187	0.996643	0.9925
8009	5.078160	0.999812	0.894872 0.000032	2.632812	0.999721	0.926654

TABLE 7: INTERLABORATORY STUDY 90-2, PART C

(Results in µg/L)

CODE	NC1	NC2	NC3	NC4	d_6-NDMA spike	DETECTOR
Spike level	Raw influent	0.450	0.550	1.020		
8001	0.013	0.444	0.526	1.100	0.666	HRMS
8002	0.019	0.3324	0.4694	0.6888	0.050	LRMS
8003	0.009	0.380	0.420	0.890	0.125	LRMS
8004	0.229	0.445	0.240	no results reported	0.099	HRMS
8005	<0.020	0.330	0.490	1.200		TEA
8006	0.037	0.300	0.396	0.566	NC1:0.040 REST:0.250	HRMS
8007	Unable to provide results for this study - new instrumentation.					
8008	Did not participate in this study.					
8009	<0.050	0.450	0.560	1.060	0.625	LRMS
8010	Did not report results					
8011	Did not report results					
MEAN	0.0194	0.3258	0.4431	0.7864		
MEDIAN	0.019	0.3324	0.4694	0.975		
STD DEV	0.0099	0.1367	0.1060	0.2490		

LEGEND: HRMS: High resolution mass spectrometer
LRMS: Low resolution mass spectrometer
TEA: Thermal energy analyzer

TABLE 8: INTERLABORATORY STUDY 90-2, PART C

Results Converted to Percent Recovery of Design Value after Blank Correction

CODE	NC2	NC3	NC4
DESIGN	0.450 µg/L	0.550 µg/L	1.020 µg/L
8001	96%	93%	107%
8002	70%	82%	66%
8003	82%	75%	86%
8004	5%	39%	
8005	71%	87%	117%
8006	58%	65%	52%
8009	94%	97%	101%
MEAN	68%	77%	88%
MEDIAN	70%	82%	94%
STD DEV	31%	20%	25%

FIG. 1: INTERLABORATORY STUDY 90–2, PART A

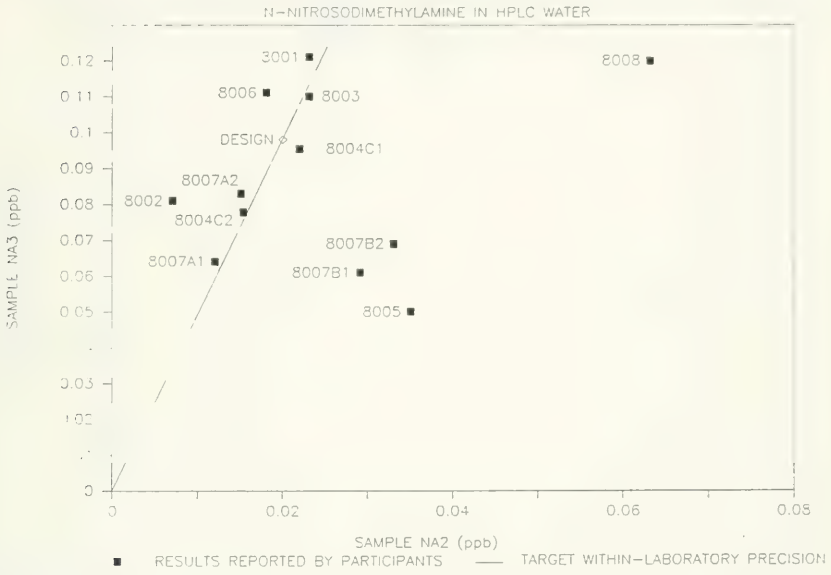


FIG. 2: INTERLABORATORY STUDY 90–2, PART A

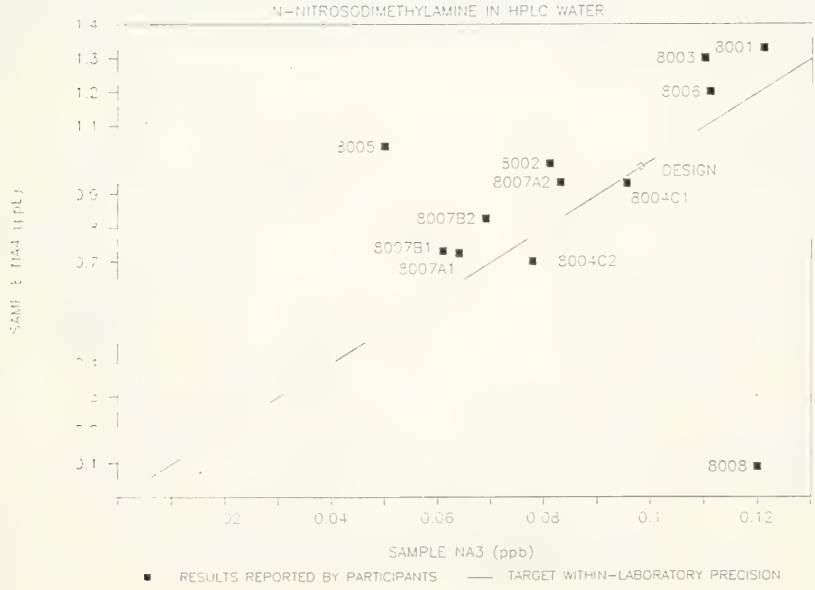


FIG. 3: INTERLABORATORY STUDY 90–2, PART B

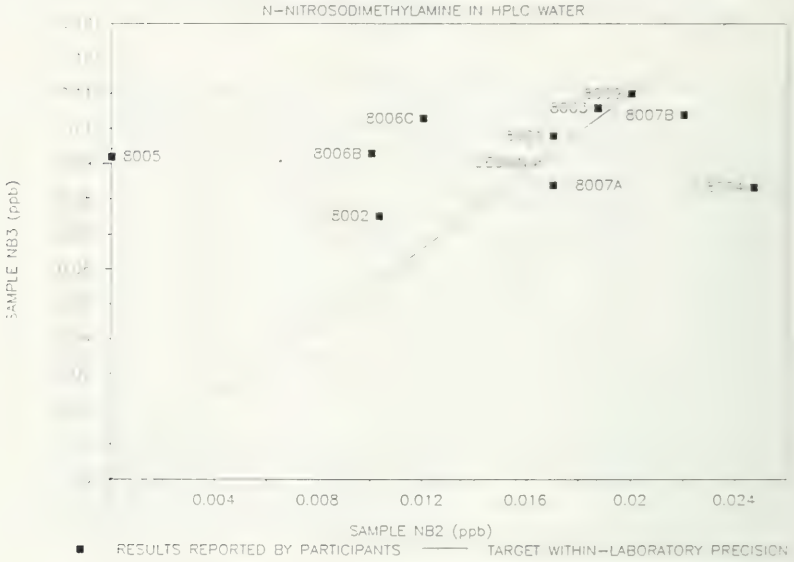


FIG. 4: INTERLABORATORY STUDY 90–2, PART B

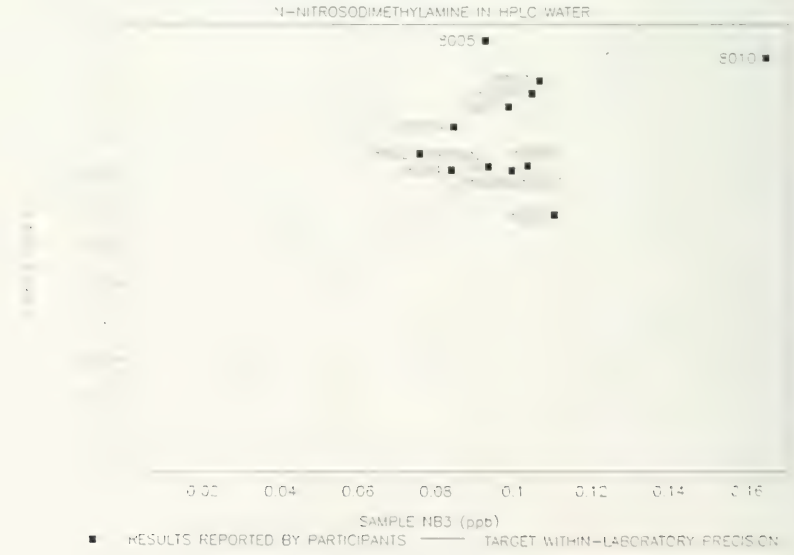


FIG. 5: INTERLABORATORY STUDY 90-2, PART B

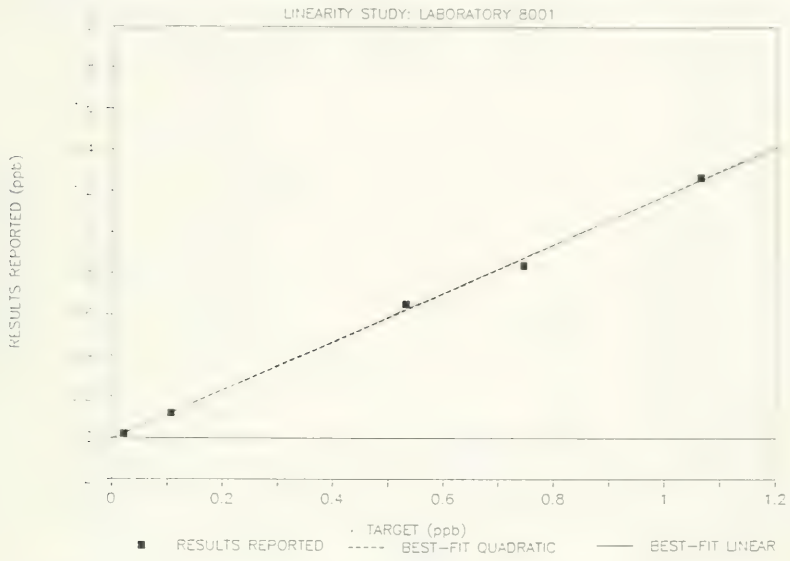


FIG. 6: INTERLABORATORY STUDY 90-2, PART B

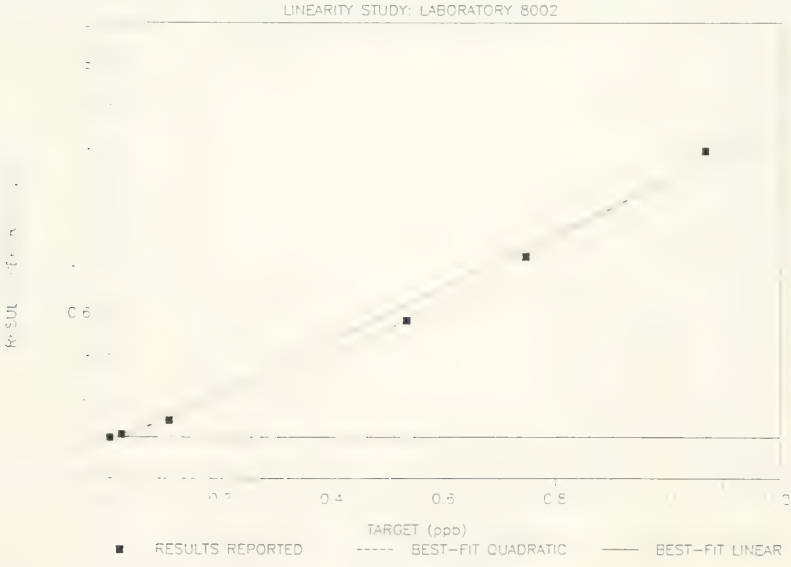


FIG. 7: INTERLABORATORY STUDY 90–2, PART B

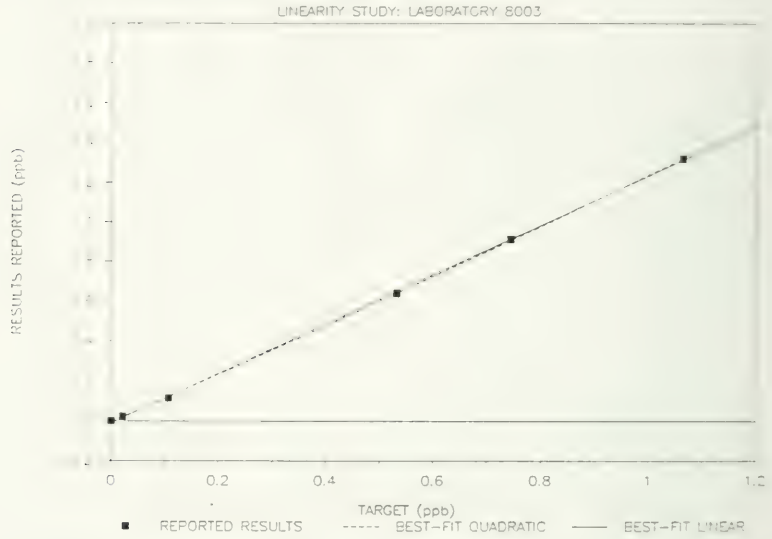


FIG. 8: INTERLABORATORY STUDY 90–2, PART B

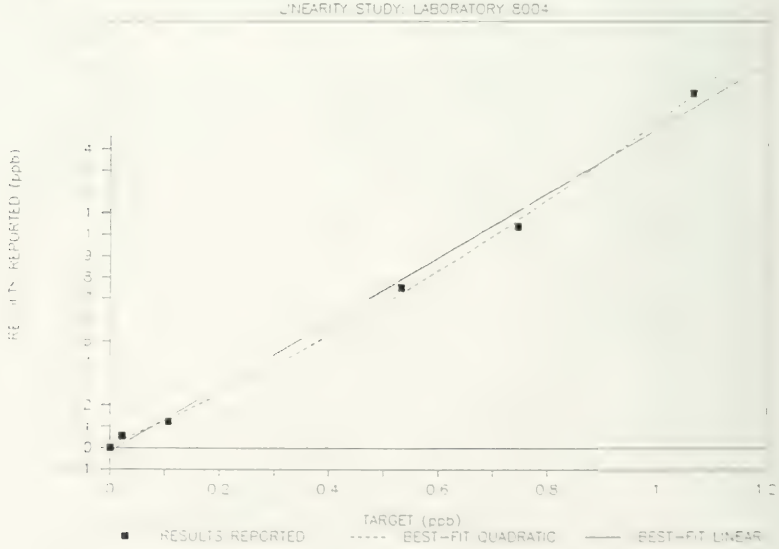


FIG. 9: INTERLABORATORY STUDY 90–2, PART B

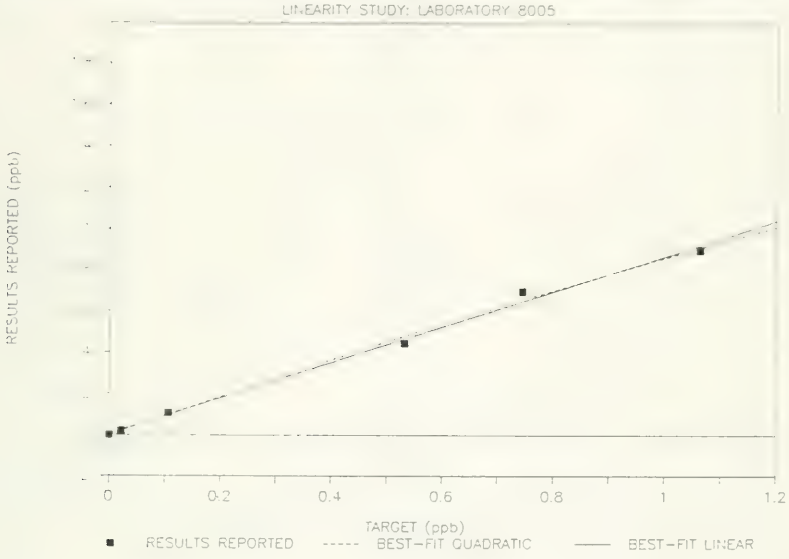


FIG. 10: INTERLABORATORY STUDY 90–2, PART B

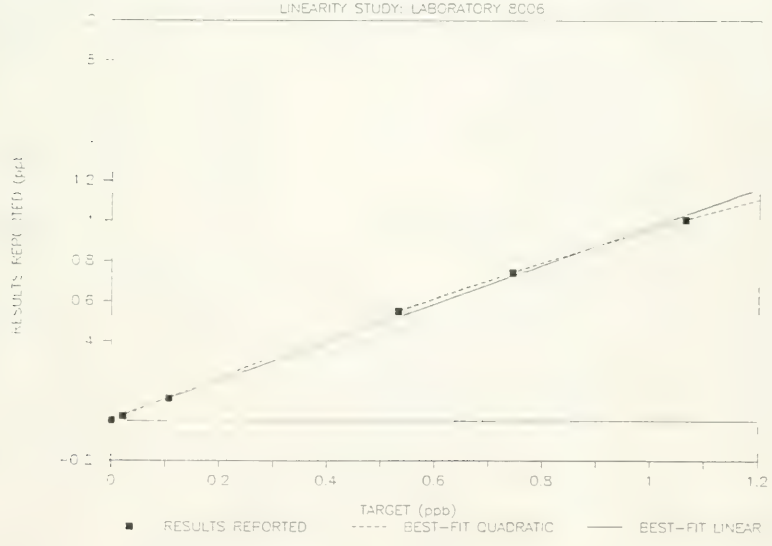


FIG. 11: INTERLABORATORY STUDY 90-2, PART B

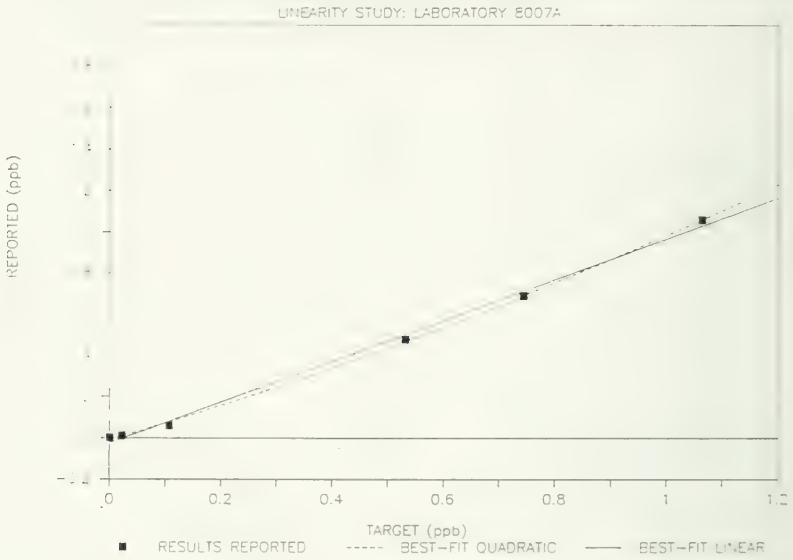


FIG. 12: INTERLABORATORY STUDY 90-2, PART B

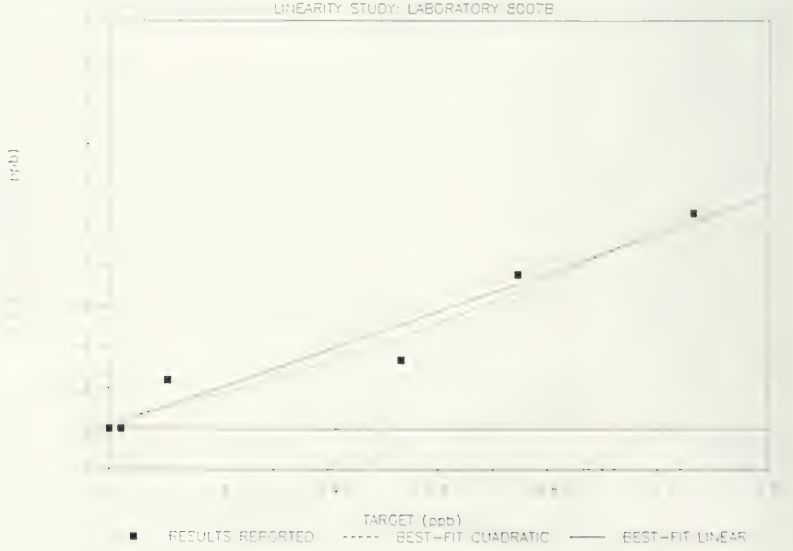


FIG. 13: INTERLABORATORY STUDY 90-2, PART B

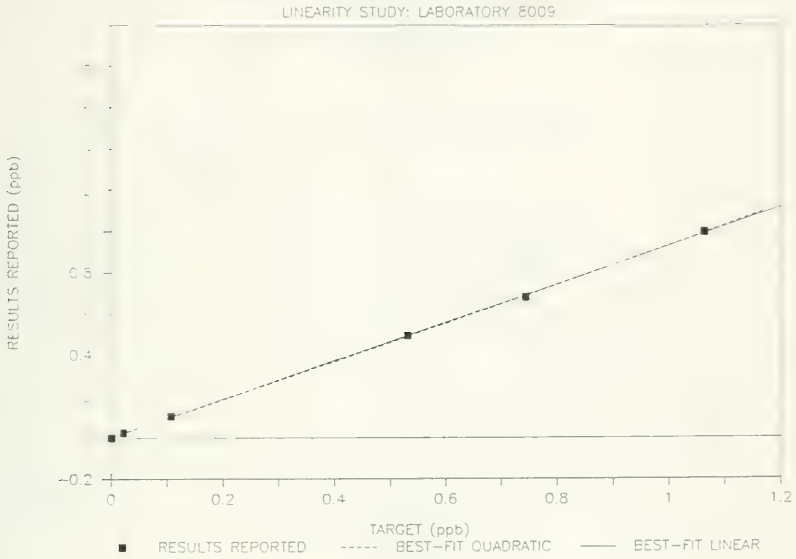


FIG. 14: INTERLABORATORY STUDY 90-2, PART C

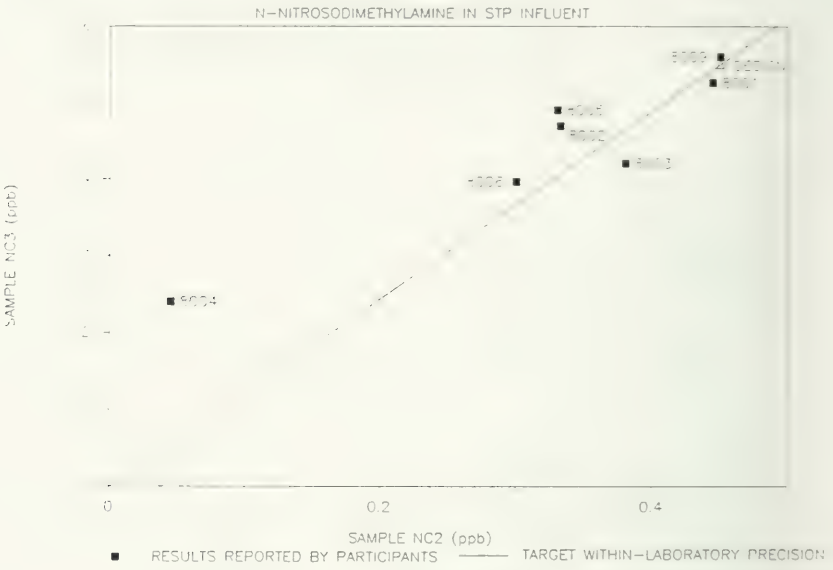
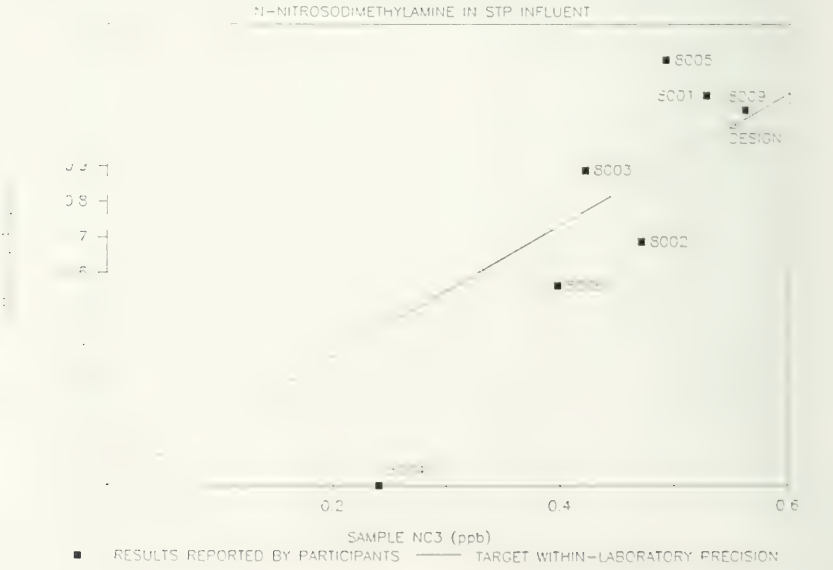


FIG. 15: INTERLABORATORY STUDY 90-2, PART C



7 APPENDIX 2: LIST OF PARTICIPANTS AND CORRESPONDENCE

Uniroyal Chemical Ltd.
Research Laboratories
120 Huron St.
Guelph, Ontario
N1H 6N3

Contact: Paul Thomson/Anthony Riggs
(519) 822-3790

Environment Ontario
Laboratory Services Branch
Mass Spectrometry Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

Contact: Vince Taguchi
(416) 235-5902

Ortech International
2395 Speakman Dr.
Mississauga, Ontario
L5K 1B3

Contact: Jack Brady
(416) 822-4111, ext. 419

Biotechnology Research Institute
6100 Royalmount
Montreal, Quebec
H4P 2R2

Contact: Michael Mancini
(514) 773-1105
Neil Stook
(613) 723-8426

Uniroyal Chemical Company, Inc.
World Headquarters
Benson Road
Middlebury, CT 06749
U.S.A.

Contact: Albert Nitowski
(203) 573-3495

Semoptics Ltd.
#7-148 Colonade Rd.
Nepean, Ontario
K2E 7R4

Contact: Pierre Coulombe
(613) 727-1698

Environment Ontario
Laboratory Services Branch
Organic Water Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1

Contact: C. David Hall
(416) 235-5910

Eli-ECO Logic International
143 Dennis St.
Rockwood, Ontario
N0B 2K0

Contact: Elizabeth Chisholm
(519) 856-9591

Environment Canada
Wastewater Technology Centre
Conservation and Protection
867 Lakeshore Rd., Box 5050
Burlington, Ontario
L7R 4A6

Contact: Robert Hong-You
(416) 336-4504

Canviro Analytical Laboratories Ltd.
50 Bathurst Dr., Unit 12
Waterloo, Ontario
N2V 2C5

Contact: Dale Sutherland/Annette Bibaud
(519) 747-2575

Concord Scientific
2 Tippet Rd.
Downsview, Ontario
M3H 2V2

Contact: Phil Fellin
(416) 630-6331

Regional Municipality of Waterloo
Engineering Laboratory
100 Maple Grove Rd.
R.R. #31
Cambridge, Ontario
N3H 4R6

Contact: Fizal Haniff/David Andrew
(519) 885-9500

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1

(416) 235-5842

February 20, 1990

**NOTIFICATION OF INTERLABORATORY STUDY 90-2:
N-NITROSODIMETHYLAMINE**

The Quality Assurance Unit of the Laboratory Services Branch will be conducting an interlaboratory variability study for the analysis of N-Nitrosodimethylamine. This study is to be conducted the week of March 5, 1990. Participating laboratories will receive four (4) samples of spiked reagent water. Analysis must be initiated within four days of receipt of samples. Results are to be reported by March 23, 1990.

Laboratories receiving this notification should contact me as soon as possible if they have any difficulties with the above schedule.

Sylvia Cussion
Laboratory Quality Audit Scientist

Laboratory Services Branch
Quality Assurance Unit
125 Resources Road
Rexdale, Ontario M9W 5L1
(416) 235-5842
FAX (416) 235-5744

March 5, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2

Please find enclosed four 1000 mL amber glass bottles. The samples are to be analyzed for N-Nitrosodimethylamine. They are labelled as follows:

Distilled water: N1 N2 N3 N4

If you are missing any of the above items, please contact me at the above phone number immediately.

As stated in the notification distributed February 20, 1990, analysis must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 degrees Celcius in the dark until ready for analysis. To ensure timely release of a summary report, results are to be submitted by March 23, 1990. A report form is included with the samples. Please identify all sample results with your lab identification number and the sample numbers described above. Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

Laboratory Services Branch
Quality Assurance Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

March 14, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2

Preliminary results from the analysis of the samples distributed on March 6, 1990, have indicated a contamination problem with the distilled water used for preparing the spiked samples. This problem has been traced to a resin cartridge. I apologize for any difficulties encountered with the analysis of the samples. However, the results from the samples are still valuable for assessing interlaboratory comparability, and I would appreciate receiving the results of the analyses.

The original design of the interlaboratory study was to assess the interlaboratory comparability at low levels (ng/L). To achieve this goal, I am distributing a second set of samples prepared in ultrapure HPLC water, that has been confirmed for the absence of contamination with N-Nitrosodimethylamine.

Please find enclosed four 1000 mL amber glass bottles. The samples are to be analyzed for N-Nitrosodimethylamine. They are labelled as follows:

Ultrapure water: NA1 NA2 NA3 NA4

If you are missing any of the above samples or they have been broken in transit, please contact me at the above phone number immediately.

As stated previously, analysis must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 ±2 degrees Celcius in the dark until ready for analysis.

To ensure timely release of a summary report, results are to be submitted by March 30, 1990. A report form is included with your lab identification number and the sample numbers described above. Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

INTERLABORATORY STUDY 90-2

REPORT FORM

MARCH 14, 1990

IDENTIFICATION CODE:

SAMPLE	RESULT	EXTRACTION VOLUME	FINAL VOLUME OF EXTRACT	INJECTION VOLUME
NA1				
NA2				
NA3				
NA4				

SAMPLE PREPARATION PRINCIPLES:

INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES:

Laboratory Services Branch
Quality Management Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1
(416) 235-5842

April 19, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2

Thank you for your participation in Interlaboratory Study 90-2, the analysis of N-Nitrosodimethylamine (NDMA) in spiked reagent water. Attached is a copy of the results received from all of the participants. The design values were as follows:

NA1	Blank
NA2	0.020 µg/L
NA3	0.098 µg/L
NA4	0.980 µg/L

Please review your results for transcription errors and report any corrections to me by April 27, 1990.

This interlaboratory study will be repeated the Week of April 30, 1990. The second study will consist of four samples prepared in ultra-pure HPLC water. Spiking levels will be similar to the levels used in the first NDMA study. Results from participating laboratories are to be reported no later than May 11, 1990.

A final report will be prepared when the second phase of this study is complete. Please contact me if there are any difficulties with the above schedule.

Your laboratory identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario M9W 5L1
(416) 235-5842
FAX (416) 235-5744

April 19, 1990

NOTIFICATION OF INTERLABORATORY STUDY 90-2:
N-NITROSODIMETHYLAMINE

The Quality Management Unit of the Laboratory Services Branch will be conducting an interlaboratory variability study for the analysis of N-Nitrosodimethylamine. This study is to be conducted the week of April 30, 1990. Participating laboratories will receive four (4) samples of spiked reagent water. Analysis must be initiated within four days of receipt of samples. Results are to be reported by May 11, 1990.

Laboratories receiving this notification should contact me as soon as possible if they have any difficulties with the above schedule.

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

April 30, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2 PART 2

Please find enclosed four 1000 mL amber glass bottles and one 5 mL amber ampoule. If you are missing any of the above samples or ampoule or they have been broken in transit, please contact me at the above phone number immediately.

PART A

The four samples are to be analyzed for N-Nitrosodimethylamine. They are labelled as follows:

Ultrapure water: NB1 NB2 NB3 NB4

Analysis of the samples must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 ±2 degrees Celcius in the dark until ready for analysis.

To ensure timely release of a summary report, results of the four samples are to be submitted by May 15, 1990. A report form is included with your lab identification number and the sample numbers described above.

PART B

The 5 mL ampoule contains a concentrated stock solution of N-Nitrosodimethylamine in methanol. It is provided as spiking material for a linearity study. Store the ampoule in a refrigerator at **4 ±2 degrees Celcius in the dark until ready for analysis. Do not prepare spiked samples until ready for analysis.**

The following amounts are to be spiked in 800 mL of pure reagent water:

20 µL 100 µL 500 µL 700 µL 1000 µL

Please analyze a reagent water blank with the above spikes. A separate report form has been included for the linearity study. Results for the linearity study are to be reported by May 25, 1990.

Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

INTERLABORATORY STUDY 90-2 PART 2

REPORT FORM PART A

APRIL 30, 1990

REPORT DUE DATE: MAY 15, 1990

IDENTIFICATION CODE:

SAMPLE	RESULT	EXTRACTION VOLUME	FINAL VOLUME OF EXTRACT	INJECTION VOLUME
NB1				
NB2				
NB3				
NB4				

SAMPLE PREPARATION PRINCIPLES:

INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES:

INTERLABORATORY STUDY 90-2 PART 2

REPORT FORM PART B

APRIL 30, 1990

REPORT DUE DATE: MAY 25, 1990

IDENTIFICATION CODE:

SPIKING LEVEL	RESULT	EXTRACTION VOLUME	FINAL VOLUME OF EXTRACT	INJECTION VOLUME
Blank				
20 µL				
100 µL				
500 µL				
700 µL				
1000 µL				

SAMPLE PREPARATION PRINCIPLES:

INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES:

Laboratory Services Branch
Quality Management Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1
(416) 235-5842

June 15, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2

Thank you for your participation in Interlaboratory Study 90-2 (Part 2), the analysis of N-Nitrosodimethylamine (NDMA) in spiked reagent water. Attached is a copy of the results received from all participants reporting results. The design values are indicated at the top of Tables I and II. Table III contains the values for the linear regression applied to the results from the Linearity Study. In all cases, a linear and quadratic fit were applied. Each participant is also provided with a plot of their own results vs. the target values for the Linearity Study. Both the linear and quadratic "best-fit" curves were drawn.

Please review your results for transcription errors and report any corrections to me by June 29, 1990.

The final segment of the NDMA interlaboratory study will be conducted the Week of June 25, 1990. The second study will consist of four samples prepared in sewage influent. Spiking levels will be designed to reflect those found in influent/effluent samples. Results from participating laboratories are to be reported no later than July 20, 1990. Please contact me immediately if you are unable to adhere to this schedule.

A final report will be prepared when this final phase of the NDMA study is complete.

Your laboratory identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

Laboratory Services Branch
Quality Management Unit
125 Resources Road
Rexdale, Ontario
M9W 5L1
(416) 235-5842
FAX (416) 235-5744

July 9, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2 PART 3

Please find enclosed four 1000 mL amber glass bottles. If you are missing any of the above samples or they have been broken in transit, please contact me at the above phone number immediately.

The four samples are to be analyzed for N-Nitrosodimethylamine. They are labelled as follows:

Sewage influent: NC1 NC2 NC3 NC4

Analysis of the samples must be initiated within four days of receipt of samples. Store all samples in a refrigerator at 4 ±2 degrees Celcius in the dark until ready for analysis.

To ensure timely release of a summary report, results of the four samples are to be submitted by August 3, 1990. A report form is included with your lab identification number and the sample numbers described above.

Please contact me if there are any problems or questions re the interlaboratory study. Thank you for your participation.

Your lab identification number is:

Sincerely,

Sylvia Cussion
Lab Quality Audit Scientist
(416) 235-5842

INTERLABORATORY STUDY 90-2 PART 3

JULY 9, 1990

REPORT DUE DATE: AUGUST 3, 1990

IDENTIFICATION CODE:

SAMPLE	RESULT	EXTRACTION VOLUME	FINAL VOLUME OF EXTRACT	INJECTION VOLUME
NC1				
NC2				
NC3				
NC4				

SAMPLE PREPARATION PRINCIPLES:

INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES:

Laboratory Services Branch
Quality Management Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1
(416) 235-5842

July 31, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2

Thank you for your participation in Interlaboratory Study 90-2 (Part 3), the analysis of N-Nitrosodimethylamine (NDMA) in spiked influent. Attached is an interim report of the results received from all participants as of this date. The design values are indicated at the top of Table I.

Please review your results for transcription errors and report any corrections to me by August 15, 1990. A final table of results will be issued when all have been received.

This was the final segment of the NDMA interlaboratory study. A final report will be prepared and distributed to all participants.

Your laboratory identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist

Laboratory Services Branch
Quality Management Unit
125 Resources Rd.
Rexdale, Ontario
M9W 5L1
(416) 235-5842

August 7, 1990

TO: PARTICIPANTS OF INTERLABORATORY STUDY 90-2, Part 3

Thank you for your participation in Interlaboratory Study 90-2 (Part 3), the analysis of N-Nitrosodimethylamine (NDMA) in spiked Elmira STP influent. Attached is a copy of the results received from participants reporting results as of August 3, 1990. The design values are indicated at the top of Table I.

Please review your results for transcription errors and report any corrections to me by August 15, 1990.

The two Ministry laboratories participating in this study (8001 and 8009) did not report any difficulties in analyzing these samples and also demonstrated accurate results. Many of the other participants reported difficulties with the analysis of the spiked influent samples, and the results are markedly lower than the design values. This is of concern to the Ministry of Environment. We wish to propose an analysts' discussion session to compare differences in methods, from extraction through instrumentation. Please contact me if you would be willing to participate in a tele-conference to attempt to resolve some of these differences. After this session, we would then conduct another interlaboratory study for NDMA in spiked Elmira STP influent.

Your laboratory identification code is:

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist